Rotational Diffusion of Neutral and Charged Solutes in 1-Butyl-3-Methylimidazolium Based Ionic Liquids: Influence of Nature of Anion on Solute Rotation

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Supporting Information

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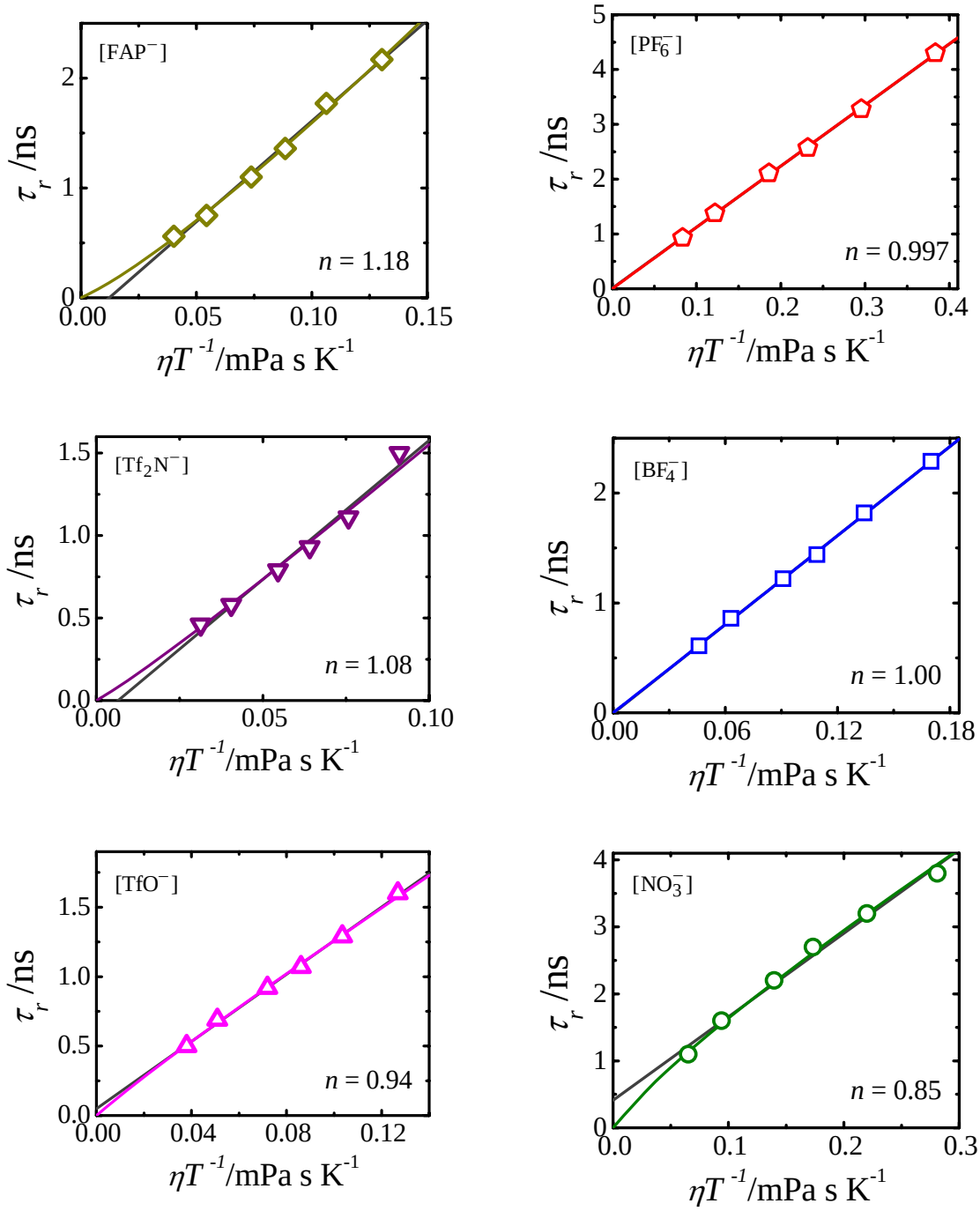

Figure 1. Plots of τ_r versus η/T for DMDPP in 1-butyl-3-methylimidazolium based ionic liquids with various anions. Linear and nonlinear fits with the degree of nonlinearity (n) are also shown in the figure.

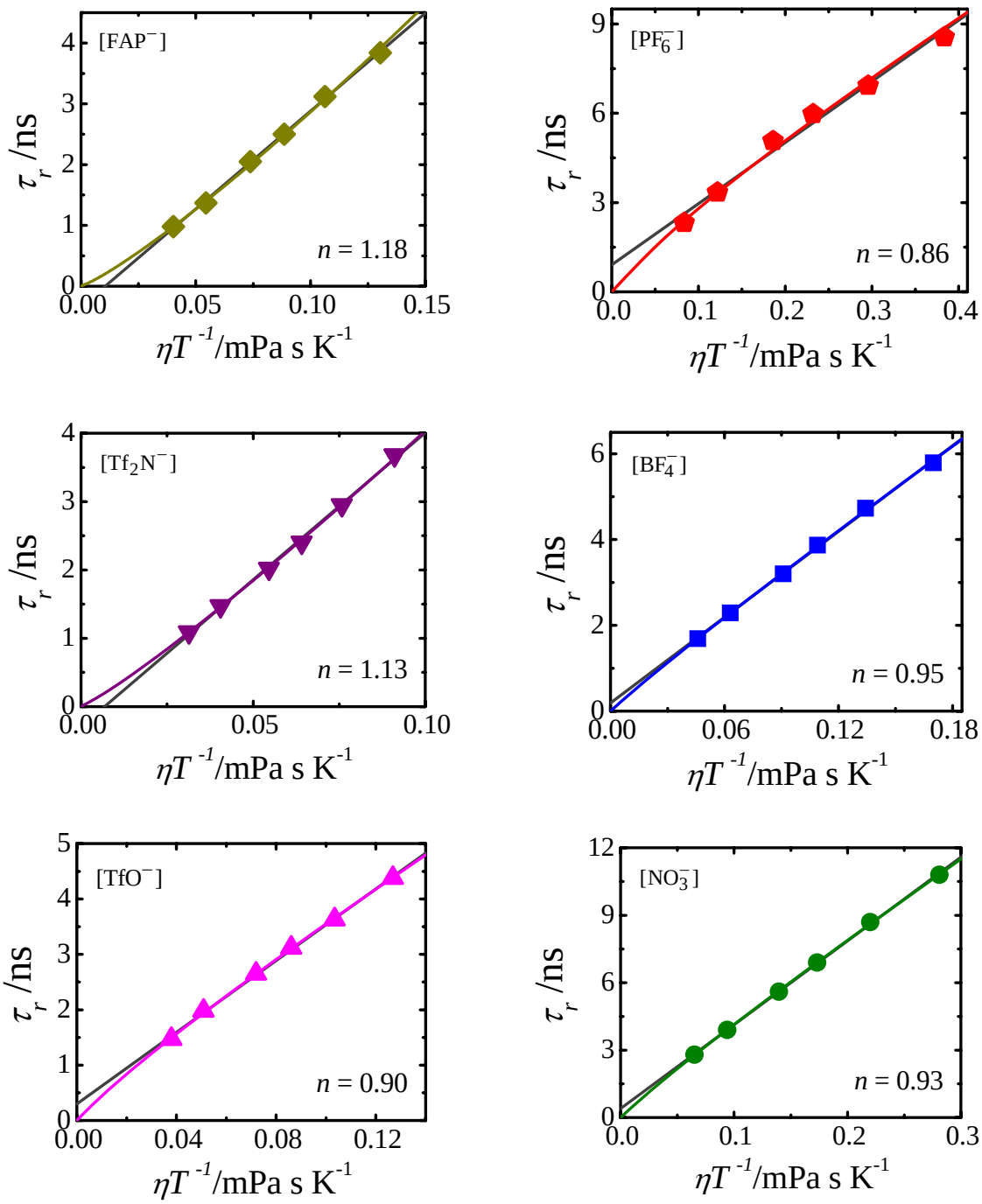

Figure 2. Plots of τ_r versus η/T for R110 in 1-butyl-3-methylimidazolium based ionic liquids with various anions. Linear and nonlinear fits with the degree of nonlinearity (n) are also shown in the figure.

TABLE 1: Reorientation Times of DMDPP and R110 in [bmim$^+$][FAP$^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		[a] τ_r / ns	[1] C_{obs}	[2] C_{obs}	[a] τ_r / ns	[1] C_{obs}	[2] C_{obs}
313	40.8	2.17	0.40	0.36	3.84	0.73	0.59
318	33.8	1.77	0.40	0.37	3.12	0.73	0.61
323	28.6	1.36	0.37	0.35	2.50	0.70	0.61
328	24.2	1.10	0.36	0.35	2.05	0.69	0.62
338	18.4	0.75	0.33	0.35	1.37	0.62	0.59
348	14.0	0.56	0.34	0.37	0.98	0.60	0.61

[a]Data taken from ref 20.

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

TABLE 2: Reorientation Times of DMDPP and R110 in [bmim$^+$][PF$_6^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		τ_r / ns	[1] C_{obs}	[2] C_{obs}	τ_r / ns	[1] C_{obs}	[2] C_{obs}
313	120	4.30	0.27	0.27	8.56	0.55	0.80
318	94.0	3.28	0.27	0.27	6.93	0.58	0.81
323	75.0	2.57	0.27	0.27	5.98	0.64	0.86
328	61.0	2.11	0.27	0.27	5.07	0.68	0.89
338	41.2	1.38	0.27	0.27	3.34	0.68	0.83
348	29.1	0.93	0.27	0.27	2.32	0.69	0.79

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

TABLE 3: Reorientation Times of DMDPP and R110 in [bmim$^+$][Tf$_2$N$^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		τ_r / ns	[1]C_{obs}	[2]C_{obs}	τ_r / ns	[1]C_{obs}	[2]C_{obs}
313	28.5	1.50	0.40	0.39	3.68	1.00	0.86
318	24.1	1.10	0.35	0.35	2.95	0.96	0.85
323	20.7	0.93	0.35	0.35	2.40	0.93	0.84
328	17.9	0.79	0.35	0.36	2.02	0.92	0.85
338	13.7	0.58	0.35	0.36	1.47	0.90	0.86
348	10.9	0.46	0.35	0.38	1.09	0.86	0.85

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

TABLE 4: Reorientation Times of DMDPP and R110 in [bmim$^+$][BF$_4^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		τ_r / ns	[1]C_{obs}	[2]C_{obs}	τ_r / ns	[1]C_{obs}	[2]C_{obs}
313	53.2	2.29	0.33	0.33	5.79	0.84	0.93
318	42.7	1.82	0.34	0.34	4.73	0.87	0.95
323	35.2	1.44	0.33	0.33	3.87	0.88	0.95
328	29.8	1.22	0.33	0.33	3.20	0.87	0.93
338	21.3	0.86	0.34	0.34	2.29	0.90	0.94
348	16.0	0.61	0.33	0.33	1.69	0.91	0.94

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

TABLE 5: Reorientation Times of DMDPP and R110 in [bmim$^+$][TfO$^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		τ_r / ns	[1]C_{obs}	[2]C_{obs}	τ_r / ns	[1]C_{obs}	[2]C_{obs}
313	39.7	1.60	0.30	0.31	4.38	0.86	1.00
318	32.9	1.29	0.30	0.31	3.63	0.87	0.99
323	27.8	1.07	0.30	0.30	3.12	0.90	1.01
328	23.6	0.92	0.31	0.31	2.65	0.91	1.01
338	17.2	0.69	0.33	0.32	1.98	0.94	1.01
348	13.2	0.50	0.32	0.30	1.47	0.95	0.99

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

TABLE 6: Reorientation Times of DMDPP and R110 in [bmim$^+$][NO$_3^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		[a] τ_r / ns	[1]C_{obs}	[2]C_{obs}	τ_r / ns	[1]C_{obs}	[2]C_{obs}
313	88.0	3.83	0.33	0.42	10.80	0.95	1.14
318	70.0	3.16	0.35	0.43	8.70	0.98	1.16
323	56.0	2.66	0.37	0.44	6.90	0.99	1.14
328	45.8	2.18	0.38	0.44	5.60	0.99	1.13
338	31.8	1.56	0.40	0.43	3.90	1.03	1.14
348	22.7	1.12	0.41	0.42	2.80	1.06	1.15

[a]Data taken from ref 19.

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

TABLE 7: Reorientation Times of DMDPP and R110 in [emim$^+$][PF$_6^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		τ_r / ns	[1]C_{obs}	[2]C_{obs}	τ_r / ns	[1]C_{obs}	[2]C_{obs}
338	27.1	0.88	0.27	0.26	2.02	0.62	0.59
348	20.3	0.65	0.27	0.26	1.39	0.59	0.58
358	15.8	0.50	0.27	0.26	1.06	0.60	0.59

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

TABLE 8: Reorientation Times of DMDPP and R110 in [hmim$^+$][PF$_6^-$] as a Function of Temperature Along with Solvent Viscosities. Boundary Condition Parameters of DMDPP and R110 are Also Given in the Table

T / K	η / mPa s	DMDPP			R110		
		τ_r / ns	[1]C_{obs}	[2]C_{obs}	τ_r / ns	[1]C_{obs}	[2]C_{obs}
313	199	6.67	0.25	0.31	14.0	0.55	1.11
318	153	4.90	0.25	0.29	12.3	0.63	1.24
323	118	3.81	0.25	0.29	9.88	0.67	1.24
328	93.7	3.19	0.27	0.30	7.95	0.69	1.20
338	61.5	1.93	0.26	0.27	5.63	0.77	1.22
348	41.8	1.50	0.30	0.31	3.85	0.79	1.14

[1] C_{obs} values obtained using eq 1.

[2] C_{obs} values obtained using eq 2.

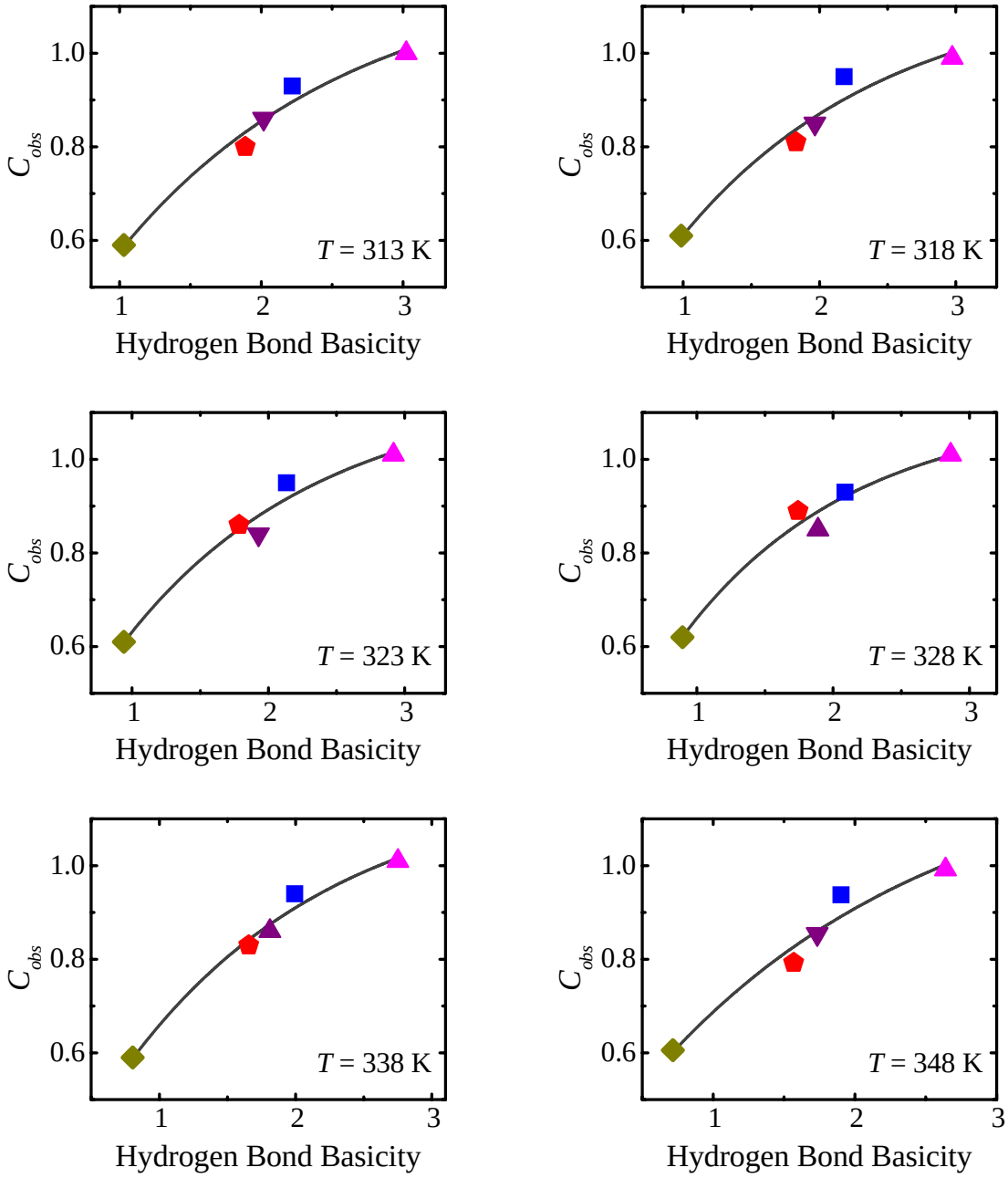

Figure 3. Plots of C_{obs} versus hydrogen bond basicity for R110 at different temperatures in 1-butyl-3-methylimidazolium based ionic liquids with the anions [FAP$^-$] (◆), [PF$_6^-$] (⬟), [Tf$_2$N$^-$] (▼), [BF$_4^-$] (■) and [TfO$^-$] (▲). C_{obs} values have been calculated using eq 2 and the lines passing through the data points are drawn as visual aid.